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(54) **Production of alkanols**

(57) A liquid phase process for the manufacture of C_{2+} alkanols by the reaction of hydrogen with carbon monoxide in the presence of a catalyst containing ruthenium, cobalt, a halogen or a halide-containing compound, and an aromatic compound substituted in adjacent ring positions by nitrogen atoms. The preferred aromatic compound is o - phenylene diamine or 3, 4-diaminotoluene.

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DESCRIPTION

PRODUCTION OF ALKANOLS

The present invention relates to a liquid phase process for the manufacture of C_{2+} alkanols.

The addition of methanol to gasoline as an octane improver and fuel extender is well known. It is also known that higher alcohols are desirable in such a fuel mixture to prevent moisture-induced phase separation of the methanol. These higher alcohols can be produced by known and established chemical processes, but it would be desirable to be able to co-produce them with methanol from synthesis gas ("syngas"), i.e., mixtures of carbon monoxide and hydrogen. Described here are catalytic processes which allow the practical formation from syngas of mixtures of methanol and higher alcohols for direct addition to gasoline.

Soluble ruthenium complexes have been reported to be active catalysts for the conversion of syngas to alcohols. Amines were reported to be promoters for the ruthenium carbonyl complexes in the production of alcohols and ethylene glycol, but they do little to increase the production of C_{2+} alcohols. (See EP-A-013008).

o-Phenylenediamine (1,2-phenylenediamine) was reported to promote the activity of ruthenium carbonyl

complex catalysts in a process for producing methanol and ethylene glycol, but the process yielded insignificant amounts of C_{2+} alcohols (S.Nakamura, T.Deguchi, T.Takano and M. Ishino, Jap.Pat. JP 59/73532). A derivative of o-phenylenediamine, benzimidazole, was also reported in the literature (Kiso, Y.; Saeki, K, Japanese Pat. JP 58/22503 A2; idem. J Organomet. Chem 1986, 303, C17 and idem. ibid. 1986, 309 C26), again to promote the activity of the ruthenium system to produce methanol and ethylene glycol but not C_{2+} alcohols.

Halides were reported to be a promoter for the ruthenium system which increases both the activity and selectivity to C_{2+} alcohols (EP-A- 0048980).

Bimetallic systems containing ruthenium and another metal were reported to be more active and/or more selective in producing certain products. Catalyst systems containing ruthenium, samarium or another rare earth element, and halides were reported to produce more C_{2+} alcohols than the system without samarium or the other rare earth elements (US-A- 4 590 216 and US-A- 4 436 837).

Catalyst systems containing ruthenium, rhodium and halides were shown to produce proportionally more ethylene glycol (EP-A- 084682).

Catalyst systems which contain ruthenium and cobalt have been reported to increase the yield of C_{2+} products, but the products are in the form of acetic acid or acetates, and the yield to alcohols is poor. In fact, the patent by Knifton and Lin (US-A-4 366 259) claimed that the catalyst systems containing ruthenium and cobalt dispersed in a molten phosphonium salt convert syngas to acetic acid selectively. Nevertheless, this reported bimetallic system, besides not being one that produces C_{2+} alcohols, did not show much improvement on the activity over the system using ruthenium alone.

Similar results were obtained in a Japanese patent (see JP 59/190935) which claimed the use of ruthenium, cobalt and halides as catalysts using phosphoric acid as solvent. Catalyst systems similar to those in the Japanese patent specification were also reported by R.A. Head and R. Whyman (US-A- 4 618 628) to convert syngas directly to higher alcohols, but those systems require a much higher pressure of 86187.5 kPa (12,500 psi) to obtain a rate equivalent to about 1.0 M/h to alcohols. Also, it is not clear from that patent specification how much acetic acid and acetates, which are less desirable products, were present in the produce of the experiments described therein.

There are many patents which claim the use of ruthenium and cobalt as catalyst systems for the conversion of methanol and syngas to ethanol. However, none disclose the use of catalyst containing ruthenium, cobalt, a halide-containing compound, and an aromatic compound substituted in adjacent (e.g., 1,2-)ring positions by nitrogen atoms.

According to the present invention there is provided a liquid phase process for the manufacture of C_{2+} alkanols by the reaction of hydrogen with carbon monoxide in the presence of a catalyst containing ruthenium, cobalt, a halogen or halide containing compound, and an aromatic compound substituted in adjacent (viz., 1,2-) ring positions by nitrogen atoms. More particularly, the invention provides a liquid phase process for the manufacture of C_{2+} alkanols by the reaction of hydrogen with carbon monoxide in the presence of a lower alkanol and a catalyst system containing ruthenium, cobalt, a halogen or halide containing compound, and an aromatic compound substituted in adjacent (such as 1,2-) ring positions by nitrogen atoms at a pressure of about 3447.5 kPa (500 psi) to about 137900 kPa (20000 psi) and at a temperature of about 100°C to about 450°C.

In a preferred embodiment of the process of the invention, the lower alkanol is produced in situ

directly from the reaction of hydrogen with carbon monoxide in the course of producing the C_{2+} alkanols.

In another preferred embodiment of the process of the invention, the nitrogen atoms substituted on the aromatic compound are amino groups or comprise part of an imidazole ring structure.

In a further embodiment of the invention, rhodium is provided in the catalyst system to enhance the formation of C_{3+} alkanols.

The invention relates to the use of catalyst systems containing a ruthenium, cobalt, halide and an ortho nitrogen di-substituted aromatic compound. In an optional embodiment, the invention encompasses the use in the catalyst system of a catalytic amount of rhodium. The invention also relates to the use of these catalyst systems to effectively convert syngas directly to alcohols and the homologation of alcohols to higher molecular weight alcohols. The catalyst systems of the invention produce alcohols selectively and very little undesirable products such as, for example, formates and acetates are produced. The catalyst systems of the invention produce a substantially higher proportion of C_{2+} alcohols than other syngas to alcohol catalyst systems.

The process of the invention is primarily directed to the production of higher alcohols which in the

context of the invention are alkanols containing 2 or more carbon atoms, for example, ethanol, propanol, isopropanol, the butanols, and the like. These higher alcohols have greater value measured in commercial terms than methanol, which in the context of the invention constitutes the lower alcohol. The invention embraces an effective process of homologating methanol to the higher alcohols. The invention also embraces an effective process of making methanol directly from syngas while simultaneously homologating some of the methanol so produced to higher alcohols, thereby conjointly producing the lower and the higher alcohols. The invention allows the incorporation to the catalyst system of rhodium thereby providing a process which generates enhanced amounts of C_{3+} alcohols, such as, for example, the propanols, butanols, pentanols, and the other members of the homologous series.

The process of the invention relates to the use of a complex catalyst system which involves a variety of diverse components yet which conjointly operate to react syngas to form methanol and homologate methanol to form one or more of the C_{2+} alkanols. The invention can also be used to homologate methanol to form the C_{2+} alkanols.

The process of the invention typically comprises the formation of a homogeneous liquid phase mixture of the catalyst system and syngas. Any heterogeneous component present in the reaction mixture would generally be a precursor component waiting to be solubilized in the carrying out of the process by reaction with another component of the reaction system such as, for example, syngas or carbon monoxide.

The ruthenium component of the catalyst system of the invention may be any ruthenium compound which can be solubilized in the reaction medium. As a rule, the ruthenium catalysts are easily obtainable as soluble components and can be used in the form of non-volatile compounds possessing high thermal stability, and exhibiting high catalytic activity at elevated temperatures. From a practical standpoint, the physical and chemical properties of the ruthenium catalyst (soluble, non-volatile, and possessing high thermal stability) permit product removal by distillation.

The selection of a suitable ruthenium compound to provide the catalytic activity for the homologation reaction and the direct reaction of syngas to alcohol is not narrowly critical. Substantially any ruthenium compound can be effectively employed to carry out these reactions. It is believed the primary

requirement for the generation of such catalysts and the requisite catalytic activity are ruthenium precursors to the catalyst which can be converted to a ruthenium carbonyl complex. The process of this invention may be practiced with a vast array of ruthenium compounds. Even in instances where the ruthenium compound is too stable for catalyzing the reaction, catalysis can be effected by including a compound which does not adversely affect the syngas and homologation reactions and stimulates the ruthenium compound to be converted to a species having catalytic activity. For example, ruthenium chloride is a sluggish catalyst but is made quite active by the addition of an alkali such as an alkali metal salt of a carboxylic acid, viz. sodium acetate. It is not presumed that simple ruthenium salt compounds are the catalyst or that many of the ruthenium compounds herein used to effect the catalytic reaction are the catalyst. The exact ruthenium containing compound or compounds that constitute the catalyst of this invention is not appreciated but what is appreciated is that many ruthenium compounds can be used to in situ generate the catalyst. The diversity of the selection of ruthenium compounds suitably employable as precursors to catalysts in the process of the invention is quite broad. Illustrative of this point,

the precursor compounds may range from supported ruthenium such as, for example, ruthenium on carbon, alumina, and the like, to ruthenium carbonyl to ruthenium(III) acetylacetonate.

Under the conditions of the raction, the ruthenium is present as a complex which contains carbon monoxide directly bonded to ruthenium (ruthenium carbonyl). The ruthenium compound which is provided to the reaction is not necessarily in a form which will effectively catalyze the reaction even if it contains a carbon monoxide ligand bonded to it. Ruthenium compounds such as, for example, ruthenium salts, oxides and carbonyl clusters may be introduced to the reaction in a condition which allows them to be solubilized, and under the conditions of the reaction they are converted into a carbonyl complex which effectively catalyzes the reaction.

The composition and structure of the ruthenium carbonyl complex which catalyzes the desired reaction is not specifically known. It may be a monoruthenium or polyruthenium compound. Illustrative of polyruthenium compounds are the well-known cluster compounds of ruthenium. However, the addition of a cluster, containing only a carbonyl ligand such as $Ru_3(CO)_{12}$ does not alone create the catalyst and, as such, cause the catalytic reaction. Some modification

of such structure is needed, possibly the destruction of the cluster structure to a mononuclear ruthenium structure. Factors to be considered in achieving the catalyst are the reaction parameters and the choice of solvent. Because varied reaction conditions and solvents, with and without promoters, result in different amounts of the desired products of the process, and different rates, efficiencies and/or yields, it is presumed that each provides a different and distinct catalytic environment.

The ruthenium-containing substances which may be employed in the practice of this invention to form the catalyst under process conditions encompass those which are described, for example, in US-A- 2 535 060 at column 2, line 38 to line 48, and ruthenium carbonyl compounds. It is not advisable to place ruthenium compounds or substances on a support material for use in the process of this invention because it offers no benefits over solubilizing such ruthenium compounds in combination with a solvent. Moreover, ruthenium deposited on a support material can be expected to be solubilized in the homogeneous liquid phase reaction system of this invention as it is contacted with carbon monoxide. Even ruthenium metal in the presence of the solvent, carbon monoxide and hydrogen can be converted to a ruthenium carbonyl

complex which is soluble. Ruthenium oxides, such as, for example, dioxide, sesquioxide, or tetraoxide, are capable under appropriate conditions of being solubilized and converted to a carbonyl complex which can be used to form the catalyst under conditions of this process. However, when using such insoluble ruthenium compounds, they must first be solubilized before the effective operation of the process of this invention.

Ruthenium carbonyl compounds (which include ruthenium carbonyl hydrides or ruthenium carbonyl clusters) are alrealdy provided with a carbonyl ligand, and under the conditions of the reaction can be sufficiently changed to achieve the desired catalytic effect. Ruthenium salts such as, for example, those of organic acids can be employed in the practice of this invention to produce the catalyst. In addition to those ruthenium compounds described in the aforementioned US-A- 2 535 060, one may employ ruthenium compounds of bidentate ligands, allyl complexes, arene complexes, halides, and alkyl complexes. The choice of ruthenium compounds is varied and not critical to this invention. A number of ruthenium complexes are known to be more stable to the presence of carbon monoxide than other ruthenium compounds and the skilled worker can determine which

particular ruthenium compound might take longer to initiate a reaction than other ruthenium compounds. On that basis, one can select for the purposes of convenience the particular ruthenium compound to be utilized in forming the catalyst. However, ruthenium which is associated with an organic molecule or complexed with carbon monoxide is most readily solubilized so as to provide the ruthenium catalyst of this process.

The ruthenium catalyst precursors may take many different forms. For instance, the ruthenium may be added to the reaction mixture in an oxide form, as in the case of, for example, ruthenium(IV) oxide hydrate, anhydrous ruthenium(IV) dioxide and ruthenium(VIII) tetraoxide. Alternatively, it may be added as the salt of a mineral acid, as in the case of ruthenium (III) chloride hydrate, ruthenium(III) bromide, ruthenium(III) iodide, tricarbonyl ruthenium(II) iodide, anhydrous ruthenium(III) chloride and ruthenium nitrate, or as the salt of a suitable organic carboxylic acid, for example, ruthenium(III) acetate, ruthenium naphthenate, ruthenium valerate and ruthenium complexes with carbonyl-containing ligands, such as ruthenium(III) acetylacetonate. The ruthenium may also be added to the reaction zone as a carbonyl or hydrocarbonyl derivative. Here, suitable examples include triruthenium dodecacarbonyl and other

hydrocarbonyls such as $H_2Ru_4(CO)_{13}$ and $H_4Ru_4(CO)_{12}$, and substituted carbonyl species such as, for example, tricarbonyl-ruthenium(II) chloride dimer, $[Ru(CO)_3Cl_2]_2$.

The cobalt component of the catalyst system can be supplied from any number of sources, many of these are known to those of ordinary skill in the art. Thus, it is not necessary for an understanding thereof to specifically enumerate every suitable type and every specific compound since any of the known compounds can be used. Cobalt promotes the formation of higher alcohols in the presence of iodide and ortho nitrogen di-substituted aromatic compound. It is generally believed that the effective form of the cobalt compound comprises cobalt carbonyl; however, the direct charging of a cobalt carbonyl complex to the reaction medium is not required. Nevertheless, descriptive of some of the useful cobalt sources are the known cobalt carboxylates such as, for example, cobalt formate, cobalt acetate, cobalt benzoate, cobalt toluate, cobalt propionate, cobalt butyrate, cobalt valerate, cobale hexanoate, cobalt cyclohexylbutyrate, and the like; the cobalt carbonyls such as, for example, dicobalt octacarbonyl, acetyl cobalt tetracarbonyl, tricobalt dodecacarbonyl, and the like including their phosphine substituted analogs many of which are known to those skilled in the art; the cobalt oxides such as, for example, cobalt oxide; cobalt hydroxide; cobalt halides such as, for

example, cobalt iodide; cobalt carbonate; cobalt bicarbonate; cobalt. Any of the known cobalt complexes can also be used. Mixtures of cobalt compounds can be used. For example, the charging of any cobalt(II) compound which can be converted in situ into dicobalt octacarbonyl and/or cobalt hydrocarbonyl under the reaction conditions employed and which causes no adverse side effects is sufficient. Various other cobalt carbonyl species in addition to those named may be produced under the reaction conditions, and may, in whole or in part, be effective catalyst system components. All such species are referred to herein as "cobalt carbonyl".

The presence of a halide in the reaction is essential for the production of higher alcohols. The halide component of the catalyst system of the invention may be supplied as a halogen compound such as, for example, hydrogen halide, alkyl- or aryl-halide, metal halide, ammonium, phosphonium, arsonium and stibonium halide, and may be the same or different from any halogen component provided in the Ru, Co or aromatic compound substituted in adjacent (viz., 1,2-) ring positions by nitrogen atoms that are components of the catalyst system. Halogen or halide compounds are generally suitable for the catalyst system, but those containing iodine and bromine are preferred, with hydrogen iodide constituting a more

preferred member. Accordingly, suitable compounds providing the halide component of the catalyst system of this invention may be selected from the following list of preferred halogen and/or halogen containing compounds:

$$RX_n$$

wherein n is 1 to 3, X is one of Cl, Br and I, R may be any alkyl alkylene or aryl group, thereby embracing compounds such as, e.g. CH_3I, C_2H_5Br, CH_3CH_2I, ICH_2CH_2I, and the like;

$$X_2 \text{ or } X^-$$

where X is one of Cl, Br, and I, thereby embracing molecules and ions as, e.g., Br_2,I_2,I^-.

$$HX$$

where X is one of Cl, Br and I, to provide such compounds as, e.g. HBr and HI.

$$AlkX$$

where X is one of Cl, Br, and I, Alk is an alkali or alkaline earth metal such as, for example, Li, Na, K, Rb, Cs, Ca, Mg, Be, Sr, and Ba to provide such compounds as, e.g., LiBr, KI and MgI_2.

$$RC(O)X$$

where X is one of Cl, Br, and I, and R may be any alkyl, alkenyl or aryl groups, to provide such compounds as, e.g. $CH_3C(O)I$, and the like;

R'_aMX, R'_bMX_2, or R'_cMX_3

where X is one of Cl, Br and I, R' is one or more of hydrogen or any alkyl- or aryl-group, M is one of N, P, As and Sb, and a, b and c represent the free valence of M, to provide such compounds as, e.g. NH_4I, PH_4I, PH_3I_2, PH_3Br_2, $(C_6H_5)_3PI_2$, and other combinations of R, M and X.

Variations in the selection of halide can have a more beneficial effect on the process of the invention. Some halides are more effective in the production of higher alcohols generally and some are more effective in producing C_{3+} alcohols specifically. For example, tetrabutylphosphonium bromide has been shown in some catalyst systems encompassed by the invention to be more effective than, e.g. KI and LiI, in producing C_{3+} alcohols.

The catalytic activity and selectivity to the higher alcohols is enhanced by providing the nitrogen substituted aromatic compound to the catalyst system of the invention. The combination of the nitrogen substituted aromatic compound and the halide component have been found essential for increasing the activity and selectivity of the catalyst system to generate higher alcohols from syngas. The aromatic compound substituted in adjacent ring positions by nitrogen atoms may be any aromatic structure soluble in the reaction medium which possesses the structure

$$\begin{array}{l} =C-N< \\ \;\;| \\ =C-N< \end{array}$$

wherein the carbon atoms form part of an aromatic ring and the double bonds represent aromatic unsaturation, and the nitrogen and its free valences constitute part of any group capable of forming an imidazone ring structure under the conditions of the syngas and homologation reactions or constitute part of an imidazole ring structure. The aromatic component of the compound may be a single or multiple ring structure. It may contain halide, alkyl, aryl, alkoxy, aroxy, and the like substitution. Apart from the fact that the aromatic compound requires the adjacent ring positioning of the nitrogen atoms, there are essentially no other limitations in structures considered important to the selection of the compound.

Simple illustrations of such nitrogen substituted aromatic compounds are ortho (o) phenylenediamine and the substituted o-phenylenediamines. Illustrative of the latter are o-phenylenediamines in which one to four hydrogen atoms on the benzene ring are substituted with groups such as, for example, halo, alkyl, cycloalkyl, aryl, aralkyl, alkoxy, hydroxy, carboxyl, amino, and nitro groups, and the remaining ring carbon atoms are bonded to hydrogen atoms. Preferred among these substituted o-phenylene diamines

are compounds in which one to four hydrogen atoms on the benzene ring are substituted with alkyl groups.

Specific examples of preferred phenylenediamines include o-phenylenediamine, tolylene-3,4-diamine, 4,5-dimethyl-o-phenylenediamine, and 2,3-diaminonaphthalene.

As pointed out above, rhodium may be added to the catalyst system of the invention to enhance the production of C_{3+} alkanols. The rhodium component of the catalyst system of the invention may be any rhodium compound which can be solubilized in the reaction medium. As a rule, the rhodium component is easily obtainable as a soluble component and can be used in the form of non-volatile compounds possessing high thermal stability, and exhibiting high catalytic activity at elevated temperatures in the catalyst system for enhancing the production of C_{3+} alcohols.

Substantially any rhodium compound can be effectively employed to enhance higher alcohol production. It is believed the primary requirement for the requisite catalytic activity of the rhodium component are rhodium precursors to the catalyst which can be converted to a rhodium carbonyl complex compounds. The process of this invention may be practised with a vast array of rhodium compounds. Even in instances where the rhodium compound is too

stable for catalyzing the reaction, catalysis can be effected by including a compound which does not adversely affect the syngas and homologation reactions and stimulates the rhodium compound to be converted to a species having catalytic activity. For example, rhodium chloride is a sluggish catalyst but is made quite active by the addition of an alkali such as an alkali metal salt of a carboxylic acid, viz. sodium acetate. It is not presumed that simple rhodium salt compounds are the catalyst or that many of the rhodium compounds herein used to effect the catalytic reaction are the catalyst. The exact rhodium containing compound or compounds that constitute the catalyst of this invention is not appreciated but what is appreciated is that many rhodium compounds can be used to in situ generate the catalyst. The diversity of the selection of rhodium compounds suitably employable as precursors to catalysts in the process of the invention is quite broad.

Under the conditions of the reaction, the rhodium is present as a complex which contains carbon monoxide directly bonded to rhodium (rhodium carbonyl). The rhodium compound which is provided to the reaction is not necessarily in a form which will effectively catalyze the reaction even if it contains a carbon monoxide ligand bonded to it. Rhodium compounds such

as, for example, rhodium salts, oxides and carbonyl clusters may be introduced to the reaction in a condition which allows them to be solubilized, and under the conditions of the reaction they are converted into a carbonyl complex which effectively catalyzes the reaction.

The composition and structure of the rhodium carbonyl complex which catalyzes the desired reaction is not specifically known. It may be a monorhodium or polyrhodium compound. Illustrative of polyrhodium compounds are the well-known cluster compounds of rhodium. However, the addition of a cluster, containing only a carbonyl ligand such as, for example $Rh_4(CO)_{12}$ does not alone create the catalyst and, as such, cause the catalytic reaction. Some modification of such structure is needed, possibly the destruction of the cluster structure to a mononuclear rhodium structure. Factors to be considered in achieving the catalyst are the reaction parameters and the choice of solvent. Because varied reaction conditions and solvents, with and without promoters, result in different amounts of the desired products of the process, and different rates, efficiencies and/or yields, it is presumed that each provides a different and distinct catalytic environment.

The rhodium-containing substances which may be employed in the practice of this invention to form the catalyst under process conditions encompass those which are described, for example, in US-A- 3 833 634. Illustrative of this point, the precursor compounds may range from supported rhodium such as, for example, rhodium on carbon, alumina, and the like, to rhodium carbonyl to chloro(1,5-cyclooctadiene)rhodium (I) dimer. It is not advisable to place rhodium compounds or substances on a support material for use in the process of this invention because it offers no benefits over solubilizing such rhodium compounds in combination with a solvent. Moreover, rhodium deposited on a support material can be expected to be solubilized in the homogeneous liquid phase reaction system of this invention as it is contacted with carbon monoxide. Even rhodium metal in the presence of the solvent, carbon monoxide and hydrogen can be converted to a rhodium carbonyl complex which is soluble. Rhodium oxides, such as, for example, dioxide, sesquioxide, or tetraoxide, are capable under appropriate conditions of being solubilized and converted to a carbonyl complex which can be used to form the catalyst under conditions of this process. However, when using such insoluble rhodium compounds, they must first be solubilized before they are

effective in contributing to the process of this invention.

Rhodium carbonyl compounds (which include rhodium carbonyl hydrides or rhodium carbonyl clusters) are already provided with a carbonyl ligand, and under the conditions of the reaction can be sufficiently changed to achieve the desired catalytic effect. Rhodium salts such as those of organic acids can be employed in the practice of this invention to produce the catalyst. In addition to those rhodium compounds described in the aforementioned US-A- 3 833 634, one may employ rhodium compounds of bidentate ligands, allyl complexes, arene complexes, halides, and alkyl complexes. The choice of rhodium compounds is varied and not critical to this invention. A number of rhodium complexes are known to be more stable to the presence of carbon monoxide than other rhodium compounds and the skilled worker can determine which particular rhodium compound might take longer to initiate a reaction than other rhodium compounds. On that basis, one can select for the purposes of convenience the particular rhodium compound to be utilized in forming the catalyst. However, rhodium which is associated with an organic molecule or complexed with carbon monoxide is most readily solubilized so as to provide the rhodium catalyst of this process.

The rhodium catalyst precursors may take many different forms. For instance, the rhodium may be added to the reaction mixture in an oxide form, as in the case of for example, rhodium(IV) oxide hydrate, anhydrous rhodium(IV) dioxide and rhodium(III) oxide. Alternatively, it may be added as the salt of a mineral acid, as in the case of rhodium(III) chloride hydrate, rhodium(III) bromide, rhodium(III) iodide, tricarbonyl rhodium(II) iodide, anhydrous rhodium(III) chloride and rhodium nitrate, or as the salt of a suitable organic carboxylic acid, for example, rhodium(III) acetate, rhodium naphthenate, rhodium valerate and rhodium complexes with carbonyl-containing ligands, such as rhodium(III) acetylacetonate. The rhodium may also be added to the reaction zone as a carbonyl or hydrocarbonyl derivative. Here, suitable examples include tetrarhodium dodecacarbonyl and hexarhodium hexadecacarbonyl, and substituted carbonyl species such as, for example, chlorodicarbonylrhodium (I) dimer, $[RhCl(CO)_2]_2$.

Under some conditions the addition of the rhodium component to the reaction results in a loss of catalytic activity. This loss can be effectively overcome by increasing the amount of the nitrogen

substituted aromatic compounds in the reaction medium, hence the catalyst system.

The quantity of ruthenium catalyst employed is not narrowly critical and can vary over a wide range. In general, the process is desirably conducted in the presence of a catalytically effective quantity of the active ruthenium species which gives a suitable and reasonable reaction rate. Reaction can proceed when employing as little as about 1×10^{-6} weight percent, and even lesser amounts, of ruthenium based on the total weight of reaction mixture (i.e., the liquid reaction mixture). The upper concentration limit can be quite high, e.g. about 30 weight percent ruthenium, and higher, and the realistic upper limit in practising the invention appears to be dictated and controlled by economics in view of the cost of ruthenium. Since the rate of conversion of syngas may be dependent upon the concentration of ruthenium employed, higher concentrations achieving higher rates, then large concentrations may prove to be a most desirable embodiment of this invention. Depending on various factors such as the promoter concentrations, the partial pressures of syngas, the total operative pressure of the reaction system, the operative temperature, the choice of solvent if one is employed, and other considerations, a catalyst

concentration of about 1 x 10^{-3} to about 20 weight percent ruthenium (contained in the complexed catalyst) based on the total weight of the reaction mixture, is generally acceptable in the practice of the invention.

The amounts of the cobalt, halide ion and ortho di-substituted aromatic nitrogen compound will be sufficient to promote the reaction of the higher alcohols. As used herein, higher alcohols mean those alcohols having at least 2 carbon atoms. Methanol is a lower alcohol. The ratios of ruthenium to cobalt to halide to ortho aromatic nitrogen compound to rhodium used in the practice of the process of the invention, may range from about 0.001 mole to about 1 mole of Ru: about 0.001 mole to about 1 mole of Co: about 0.001 mole to about 1 mole of halide (halide ion content); about 0.1 mole to about 10,000 moles, preferably about 10 to about 1,000 moles, of the ortho di-substituted aromatic nitrogen compound; and 0 mole to about 1 mole of rhodium.

The present reaction is carried out in an atmosphere of carbon monoxide and hydrogen. H_2/CO mole ratio of the syngas provided to the reaction may range from about 0.1:1.0 to about 10:1.0, most preferably 0.2:1.0 to 5:1.0. Often it will be convenient to use approximately equimolar ratios, or whatever ratios are conveniently available in

synthesis gas. The reaction to produce ethanol preferably utilizes 2 moles hydrogen per mole of carbon monoxide, but is not necessary to have the reactants present in stoichiometric ratio. The carbon monoxide contributes to catalyst stability and appreciable carbon monoxide pressure is therefore generally used such as about 3447.5 kPa (500 psi) to about 137900 kPa (20,000 psi) or more, and preferably the reaction is carried out under a total pressure of at least about 6895 kPa to about 103425 kPa (1,000 to 15,000 psi) and often conveniently at about 13790 kPa to about 34475 kPa (2000 to 5000 psi). The sum of the carbon monoxide and hydrogen pressures often constitute approximately the total pressure, and the aforesaid ranges apply to this sum.

The temperature at which the reaction is conducted may be as low as about 100°C to about 400°C. The more preferable temperature may range from about 180°C to about 260°C.

The catalytic reaction can be operated with or without a liquid solvent. When a liquid solvent is used, the solvent can be any organic compound, such as saturated or unsaturated hydrocarbon, alcohols, acetates, ethers, acids, amines, or low-melting ammonium or phosphonium salts, etc. The catalyst can operate without a solvent because o-phenylenediamine is a low-melting solid and can function as a solvent

itself when melted.

The process is effected for a period of time sufficient to produce the desired alcohol products. In general, the residence time to produce the desired products can vary from minutes to a number of hours, e.g. from a few minutes to 24 hours, and longer. It is readily appreciated that the residence period (time) will be influenced to a significant extent by the reaction temperature, the concentration and choice of promoters, ruthenium source, the total gas pressure and the partial pressure exerted by its components, the concentration and choice of solvent, and other factors. The synthesis of the desired product(s) by the reaction of hydrogen with carbon monoxide is suitably conducted under operative conditions which give reasonable reaction rates and/or conversions.

The process can be executed in a batch, semi-continuous, or continuous fashion. The reaction can be conducted in a single reaction zone or a plurality of reaction zones, in series or in parallel, or it may be conducted intermittently or continuously in an elongated tubular zone or series of such zones. The material of construction should be such that it is inert during the reaction and the fabrication of the equipment should be able to withstand the reaction temperature and pressure. The reaction zone can be fitted with internal and/or external heat exchanger(s)

to thus control undue temperature fluctuations, or to prevent any possible "runaway" reaction temperature due to the exothermic nature of the reaction. In preferred embodiments of the invention, agitation means to vary the degree of mixing of the reaction mixture can be suitably employed. Mixing induced by vibration, shaker, stirrer, rotatory, oscillation, ultrasonic, etc., are all illustrative of the types of agitation means which are contemplated. Such means are available and well-known to the art.

The catalyst system may be initially introduced into the reaction zone batchwise, or it may be continuously or intermittently introduced into such zones during the course of the synthesis reaction. Means to introduce and/or adjust the reactants, either intermittently or continuously, into the reaction zone during the course of the reaction can be conveniently utilized in the process especially to maintain the desired molar ratios of, and the partial pressures exerted by, the reactants.

As intimated previously, the operative conditions can be adjusted to optimize the conversion of the desired product and/or the economics of the process. In a continuous process, for instance, when it is preferred to operate at relatively low conversions, it is generally desirable to recirculate unreacted

synthesis gas with or without make-up carbon monoxide and hydrogen to the reactor. In addition, methanol or higher alcohols formed by the process can be recycled or maintained in the reactor so as to homologate them to higher boiling alcohols. Recovery of the desired product can be achieved by methods well known in the art such as, for example, by distillation, fractionation, extraction, and the like. A fraction comprising catalyst complex, generally contained in by-products and/or the solvent, can be recycled to the reaction zone, if desired. All or a portion of such fraction can be removed for recovery of the catalyst system components values or regeneration thereof, if necessary. Fresh catalyst components and/or solvent, can be intermittently added to the recycle stream or directly to the reaction zone, if needed.

The present invention will now be further described by reference to, but in no manner limited to, the following Examples.

EXAMPLE 1

A catalyst system containing 4.7 mmoles of $Ru_3(CO)_{12}$, 7.0 mmoles of $Co_2(CO)_8$, 30 mmoles of KI, and 92 mmoles of o-phenylenediamine was charged to a 300 millilitres autoclave along with 37.5 millilitres of diphenyl ether. The autoclave was purged with nitrogen and then with syngas. After it was

pressurized with 6895 kPa (1000 psi) of 1:1 CO/H_2 syngas, the autoclave was heated to the reaction temperature of 230°C. The pressure was then increased to 34475 kPa (5000 psi) and it was kept within ± 1379 kPa (± 200 psi) of 34475 kPa (5000 psi) by periodically repressurizing the system as gas uptake took place. After 3.0 hours, the system was cooled rapidly by a cooling coil to room temperature. After releasing the pressure, the liquid was analyzed by gas chromatography and shown to contain 12.7 grams (397 mmole) of methanol, 6.45 grams (140 mmole) of ethanol, 0.48 gram (8 mmole) n-propanol, 0.1 gram (1 mmole) of n-butanol, 0.55 gram (9 mmole) ethylene glycol, and 0.25 gram (4 mmole) of methyl acetate. The average rate to total liquid products was 5.0 moles/hour. Selectivity to alcohols was 98% by mole determination.

EXAMPLE 2

An experiment using the same catalyst system as in Example 1 but using 45 millilitres of tetrahydrofuran as solvent in place of diphenyl ether was carried out according to the procedure described in Example 1. GC analysis showed the formation of 11.2 grams (350 mmoles) of methanol, 5.0 grams (109 mmoles) of ethanol, 0.3 gram (5 mmoles) of n-propanol, 0.1 gram (1mmole) of methylacetate, and 0.5 gram (8 mmoles) of ethylene glycol.

Example 3

An experiment using the same catalyst system as in Example 1 but using 35 millilitres of sulfolane as solvent in place of diphenyl ether was carried out according to the procedure described in Example 1 with a reaction time of 2.0 hours. GC analysis showed the formation of 2.4 grams (75 mmoles) of methanol, 4.6 grams (100 mmole) of ethanol, 0.7 gram (12 mmoles) of n-propanol, and 0.1 gram (1 mmole) of methyl acetate.

Example 4

An experiment using the same catalyst system as in Example 1 but using 45 millilitres of ethanol as solvent in place of diphenyl ether was carried out according to the procedure described in Example 1. GC analysis showed the formation of 11.5 grams (359 mmoles) of methanol, 3.6 grams (78 mmoles) of ethanol (net gain), 2.12 gram (35 mmoles) of n-propanol, and 0.35 gram (5 mmoles) of n-butanol.

Example 5

An experiment using the same catalyst system as in Example 1 but using 45 millilitres of methanol as solvent in place of diphenyl ether was carried out according to procedure described in Example 1. GC analysis showed a loss of 5.0 grams (156 mmoles) of methanol and the formation of 11.4 grams (247 mmoles of ethanol, 1.2 gram (20 mmoles) of propanol, 0.2 gram (3 mmoles) of n-butanol and 0.4 gram (5 mmoles) of methyl acetate.

EXAMPLE 6

An experiment using the same catalyst system and solvent as in Example 1 was carried out according to the procedure described in Example 1 except using 27580 kPa (4000 psi) as the maximum pressure. GC analysis showed the formation of 8.4 grams (263 mmoles) of methanol, 4.3 grams (94 mmoles) of ethanol, 0.3 gram of n-propanol (5 mmoles) and 0.1 gram (1 mmole) of methyl acetate.

EXAMPLE 7

An experiment using the same catalyst system and solvent as in Example 1 was carried out according to the procedure described in Example 1 except using 20685 kPa (3000 psi) as the maximum pressure. GC analysis showed the formation of 4.7 grams (147 mmoles) of methanol, 0.64 gram (139 mmoles) of ethanol, and 0.1 gram (1 mmole) of methyl acetate.

EXAMPLE 8

An experiment using the same catalyst system and solvent as in Example 1 was carried out according to the procedure described in Example 1 except using 13790 kPa (2000 psi) as the maximum pressure. GC analysis showed the formation of 2.4 grams (75 mmoles) of methanol, 0.1 gram (2 mmoles) of ethanol and 0.1 gram (1 mmole) of methyl acetate.

EXAMPLE 9

An experiment using the same catalyst system as in Example 1 and using the solvent THF was carried out according to the procedure described in Example 1 except at an operating temperature of 245°C. GC analysis showed the product contained 9.9 grams (309 mmoles) of methanol, 6.0 grams (130 mmoles) of ethanol, 0.50 gram (8 mmoles) of n-propanol, 0.3 gram (4 mmoles of n-butanol, 0.1 gram (1 mmole) of methyl acetate and 0.2 gram (3 mmoles) of ethylene glycol.

Example 10

An experiment using the same catalyst system as in Example 1 and using the solvent THF was carried out according to the procedure described in Example 1 except at an operating temperature of 215°C. GC analysis showed the formation of 5.6 grams (175 mmoles) of methanol, 1.8 gram (39 mmoles) of ethanol, 0.2 gram (3 mmoles) of n-propanol, 0.2 gram (3 mmoles) of methyl acetate, 0.5 gram (8 mmoles) of ethylene glycol.

Examples 11-15

These examples demonstrate effects on the amounts of products formed using different solvents. The catalyst system contains 14 mmoles of Ru, 14 mmoles of Co, 93 mmoles of o-phenylenediamine, and 30 mmoles of KI in 40 grams of the solvent. Experiments were carried out at 34475 kPa (5000 psi) of 1:1 syngas, at 230°C.for 3.0 hours unless further specified.

Table 1.

Ex.	Solv.	MeOH	C_{2+} ROH	Other Ox[3]	% ROH	% C_{2+} ROH	Rate
11	Phenyl ether	12.7 g	7.1 g	0.8 g	96%	35%	5.0 M/h
12	THF	11.2 g	5.3 g	0.6 g	96%	38%	3.5 M/h
13	Sulfolane[1]	2.4g	5.3 g	0.1 g	99%	68%	2.1M/h
14	Ethanol	11.5 g	6.0 g[2]	0.8 g	96%	33%	3.3 M/h
15	Methanol	-5.0g	12.8 g	0.4 g	97%[4]	97%	0.8 M/h[5]

1. 2.0 hours reaction time
2. net gain of ethanol.
3. Other oxygenated liquid products.
4. No net methanol formation
5. Rate directly from syngas only; Rate to C_{2+} alcohols is 2.0 M/h.

Examples 16-19

These Examples, 16-19, are taken from Examples 1 and 6-8, respectively, to demonstrate the effect of different syngas pressures on the amount of alcohol product formed. As indicated previously, the catalyst system contained 14 mmoles of Ru, 14 mmoles of Co, 93 mmoles of o-phenylenediamine, and 30 mmoles of KI in 37.5 millilitres of diphenyl ether.

Table 2

Example	Pressure kPa	Pressure psi	MeOH	C_{2+} ROH	Other Ox[6]	% ROH	% C_{2+} ROH	Rate Total
16	34475	5000	12.7 g	7.1 g	0.80 g	96%	35%	5.0 M/h
17	27580	4000	8.4 g	4.6 g	0.1 g	99%	35%	3.2 M/h
18	20685	3000	4.7 g	.64 g	0.1 g	98%	12%	1.4 M/h
19	13790	2000	2.4 g	0.1 g	0.1 g	96%	4%	0.7 M/h

6. Other oxygenated liquid products.

Examples 20-22

These Examples demonstrate the amount of products formed at different temperatures. The catalyst system contained 14 mmoles of Ru, 14 mmoles of Co, 93 mmoles of o-phenylenediamine, and 30 mmoles of KI in 45 millilitres of THF.

Table 3.

Example	Temperature	MeOH	C_{2+} ROH	Other Ox[7]	% ROH	% C_{2+} ROH	Rate Total
20	245° C.	9.9 g	6.8 g	0.3 g	98%	40%	3.5 M/h
21	230° C.	11.2 g	5.3 g	0.8 g	96%	31%	3.5 M/h
22	215° C.	5.6 g	2.0 g	0.7 g	92%	24%	1.7 M/h

7. Other oxygenated liquid products.

Examples 23-24

These Examples demonstrate the use of tetra-n-butylphosphonium bromide as a solvent and as a halide source, or as both in the practice of the process of the invention.

Table 4.

Example	23	24
Catalyst	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$
mmol	4.7	4.7
solvent	$P(n\text{-}Bu)_4Br$	DMEU[10]
mL	38	38
additive	$Co/P(n\text{-}Bu)_4Br$/o-PhDA[8]	$Co/P(n\text{-}Bu)_4$/o-PhDA
mmole	7.0/118/93	7.0/59/93
pres. kPa (psi)	27580 (4000)	27580 (4000)
Temp. °C	230	230
Time, hrs.	1.5	1.5
H_2/CO	1.0	1.0
MeOH,g	3.1	4.0
EtOH,g	3.5	3.1
n-PrOH,g	2.6	2.0
n-BuOH,g	0.7	0.4
Acetates	0.5	1.2
Tot.Prod.,g	10.4	10.7
Rate,total, M/h	3.0 M/Kg-h[9]	4.3
C_{2+} alcohols %	56(23% C_{3+})	43 (16% C_{3+})

8. o-phenylenediamine
9. Rate expressed in moles of products per kilogram of $P(n\text{-}Bu)_4Br$
10. 1,3-dimethylethyleneurea

Examples 25 - 28

These Examples demonstrate the use of rhodium (as rhodium carbonyl) as an additional component of the catalyst system.

Table 5.

Example	25	26	27	28
Catalyst	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$
mmol	4.7	4.7	4.7	4.7
solvent	1,3-DMEU	1,3-DMEU	1,3-DMEU	1,3-DMEU
mL	38	38	38	38
Additive	Co/Rh/LiI/3,4-DAT[11]	Co/Rh/LiI/3,4-DAT	Co/Rh/KI/3,4-DAT	Co/Rh/KI/3,4-DAT
mmole	4.4/0.5/30/93	7.0/1.0/30/93	7.0/1.0/30/93	7.0/1.0/30/93
pres. kPa (psi)	34475 (5000)	34475 (5000)	34475 (5000)	34475 (5000)
Temp., °C	230	230	230	230
Time, hrs.	1.5	1.5	1.5	3.0
H_2/CO	1.0	1.0	1.0	1.0
MeOH,g	7.3	5.9	5.6	4.9
EtOH,g	5.8	6.5	5.7	10.2
n-PrOH,g	0.5	1.0	0.9	2.1
N-BuOH,g	0.3	0.6	0.4	1.6
Acetates	0.5	0.9	0.9	2.3
Tot.Prod., g	14.4	13.9	13.5	21.1
Rate, total, M/h	6.5	6.3	5.9	4.04
C_{2+} alcohols %	37 (3.5% C_{3+})	46 (7% C_{3+})	43 (6% C_{3+})	61 (12% C_{3+})

11. 3,4-diaminotoluene

In the above, the term "Rate," unless otherwise indicated, means the rate of production of alcohols expressed in terms of number of moles of products per litre of catalyst solution per hour of reaction time.

CLAIMS

1. A liquid phase process for the manufacture of C_{2+} alkanols by the reaction of hydrogen with carbon monoxide in the presence of a catalyst containing ruthenium, cobalt, a halogen or halide containing compound, and an aromatic compound substituted in adjacent ring positions by nitrogen atoms.

2. A process as claimed in claim 1 in which hydrogen is reacted with the carbon monoxide in the presence of a lower alkanol at a pressure of about 3447.5 kPa (500 psi) to 137,900 kPa (20,000 psi) and at a temperature of about 100°C to about 450°C.

3. A process as claimed in claim 2 in which the lower alkanol is produced in situ directly from the reaction of hydrogen with carbon monoxide.

4. A process as claimed in any of claims 1 to 3 in which the ruthenium and cobalt are in the form of carbonyl complexes.

5. A process as claimed in any of claims 1 to 4 in which rhodium is provided to the reaction.

6. A process as claimed in claim 5 in which the ruthenium, cobalt and rhodium are in the form of carbonyl complexes.

7. A process as claimed in any of claims 1 to 6 in which the lower alkanol contains less carbon atoms than the C_{2+} alkanols being produced.

8. A process as claimed in any of claims 1 to 7 in which the halogen or halide containing compound contains at least one of chlorine, bromine and iodine.

9. A process as claimed in any of claims 1 to 8 in which the halogen compound and the aromatic compound are the same.

10. A process as claimed in any of claims 1 to 9, in which the reaction is effected in a liquid phase reaction mixture.

11. A process as claimed in claim 10 in which the liquid phase reaction mixture is homogeneous.

12. A process as claimed in any of claims 1 to 11 which is carried out continuously.

13. A process as claimed in any of claims 1 to 12 in which the aromatic compound substituted in adjacent ring positions by nitrogen atoms is an aromatic structure soluble in the reaction medium which possesses the structure

$$\begin{array}{l} =\mathrm{C}-\mathrm{N}< \\ \;\;\,| \\ =\mathrm{C}-\mathrm{N}< \end{array}$$

wherein the carbon atoms form part of an aromatic ring and the double bonds represent aromatic unsaturation, and the nitrogen and its free valences constitute part of any group capable of forming an imidazole ring structure under the conditions of the syngas and homologation reactions or constitute part of an imidazole ring structure.

14. A process as claimed in claim 13 in which the aromatic compound substituted in adjacent ring positions by nitrogen atoms is ortho-phenylenediamine.

15. A process as claimed in claim 13 in which the aromatic compound substituted in adjacent ring positions by nitrogen atoms is 3,4-diaminotoluene.

16. A process for the manufacture of C_{2+} alkanols substantially as hereinbefore described with particular reference to any of the foregoing Examples.

17. C_{2+} alkanols whenever produced by a process as herein described and claimed.

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